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Forbidden Lines

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I. INTRODUCTION

ONE of the most fundamental laws of spectrum analysis is the Ritz combination principle, a law which was developed early in the history of the analysis of spectra. This principle states that the frequencies, or wave numbers, of all of the lines of the spectrum of a given atom or ion can be expressed as the differences between a relatively small number of term values. According to our present picture of atomic structure this principle is interpreted by stating that the electrons of an atom can exist in certain states or modes of vibration each of which has a definite energy. A line of the spectrum of the atom is emitted when the atom changes from one state to another, each particular pair of states corresponding to a different line. The energy of the line emitted comes from the difference in the energy of the two states or terms between which the transfer occurs and the frequency of the line is equal to this energy difference divided by Planck's constant h. The term values whose differences give the frequencies of the observed lines are therefore proportional to the energies of the various possible states of the atom.

While the frequencies of all lines can be expressed as the differences between a set of terms the converse is not always true, i.e., all differences between the known terms of an atom are not represented by observed lines. Early in the development of spectrum analysis it was, however, found possible to set up simple empirical selection rules which enable one to predict satisfactorily whether the difference between a given pair of terms will correspond to an observed line or not. Stated in their complete form and in terms of the quantities used to describe a state in our present atomic structure theory, the general conditions that must be satisfied for the appearance of an observed line are:

First, the azimuthal (or orbital angular momentum), quantum number, l, of one electron in the atom must change by ± 1 while those of all other electrons must remain the same or in certain rather rare instances change by ± 2. As first suggested by Laporte, another formulation of this rule may be made by dividing all terms or states of an atom into two classes, those in which the arithmetical sum of the azimuthal quantum numbers of all electrons in the atom is odd, and those in which the sum is even. This selection rule then states that transitions may occur from odd to even, or even to odd terms but not between two terms of the same class or parity.

Second, the so-called inner quantum number, J, which represents the total angular momentum of the atom (obtained by adding vectorially all orbital and spin angular momenta) must change by 0, or ± 1, a change of 0 to 0 being excluded.

In the case of atoms that are subject to Russell-Saunders or LS coupling two additional conditions must be satisfied for a line to appear. These special selection rules are that the vector sum L of all of the azimuthal quantum number vectors l must change by 0 or ± 1 and that the vector sum S of all the electron spins must not change. This latter condition means that intercombination lines, i.e., transitions between terms of different multiplicities are forbidden. Since no actual atom follows exactly the Russell-Saunders coupling but merely approaches it with varying degrees of approximation, these special selection rules are not rigorously followed, particularly by the heavier atoms.

Lines or transitions satisfying all the selection rules that apply to the atom concerned are classed as permitted lines while all others are spoken of as *forbidden lines*. This division of all possible lines into just two classes, i.e., permitted and forbidden, is obviously inadequate to describe completely the appearance of spectrum lines. Thus on the one hand recent studies of laboratory and astronomical spectra have shown that a few of the forbidden lines may appear strongly under certain extreme conditions of excitation. On the other hand even a most casual inspection of any spectrum shows that the observed permitted lines have a very wide range of intensities. The quantitative measures of line intensities by Burger, Dorgelo, Ornstein, Harrison and others, made in 1924 and the following years, emphasized these differences and made acute the necessity of a more quantitative designation of the intensity of spectrum lines.

II. Line Intensities

Neglecting any losses due to self-absorption, the intensity or energy of a given spectrum line is equal to the number of quanta of that radiation emitted per unit time by the source multiplied by the energy of each quantum which, of course, is equal to h times the frequency ν. Two principal factors enter into the determination of the number of quanta emitted. These are, first, the number of atoms, N, arriving in the upper or initial state of the transition, or line, per unit time and, second, the fraction of these atoms that drop to the lower state with the emission of the particular line considered.

The first of these factors depends largely on the excitation potential of the upper state taken in connection with the physical conditions present in the source. This factor will be considered in the discussion of the detailed structure of various atoms and of the physical conditions present in the astronomical objects where the forbidden lines are observed.

The second of these factors is obviously equal to the ratio of the probability (A_1) of the transition with the emission of the line considered, to the sum of the probabilities of all possible means of removal from the given upper state. The principal other means of removal are: First, the emission of other lines by transitions to other lower states of the atom. Let the probabilities of these be A_2, A_3, A_4, etc. Second, the removal of the atom from the upper state by a collision of either the first or the second kind, with another atom or an electron. In a collision of the first kind the atom takes up kinetic energy from the colliding particle and is thereby raised to a still higher state. In a collision of the second kind, the atom is dropped to a lower state at the time of collision, the energy difference being used to increase either the kinetic energy of the colliding particles or the potential energy of the other atom or both. Obviously the probability B of this mechanism will depend to a large extent on the physical conditions in the source. Third, the removal of the atom from the state by the absorption of radiation thereby raising the atom to a still higher state. The probability, C, of this absorption will depend, of course, on the density of radiation. Collecting these terms the intensity of the line may then be written

$$I = NA_1h\nu/(B+C+A_1+A_2+A_3\cdots). \quad (1)$$

For certain purposes it is convenient to express this intensity in terms of n the average number of atoms in the upper state at any one time. The intensity is then

$$I = nA_1h\nu. \quad (2)$$

That (2) is equivalent to (1) is at once evident since in the steady state the number of atoms in the upper state, n, is equal to the rate at which atoms are arriving in this state, N, divided by the total probability $(B+C+A_1+A_2+A_3\cdots)$ that any atom will be removed from the state in unit time.

III. Transition Probabilities

The transition probability A[1] of any jump between two states is usually defined as the reciprocal of the average time that the atom would remain in the upper state if the transition under consideration were the only path by which the atom could be removed from this upper state. A calculation[2, 3] of the transition probability of any transition normally comes out in a series the first term of which has the form of the radiation from an electric dipole, the second term from a quadrupole and higher terms from higher multipoles. All terms except the first are often split into parts. Thus the second term may be considered as being made up of two parts the first of which corresponds strictly to electric quadrupole radiation while the second represents magnetic dipole radiation. Unfortunately in much of the early literature a certain amount of ambiguity exists as to whether the calculations given apply to the complete second or third terms of the series or to the electric quadrupole or octopole parts only.

These calculations further show that, when the empirical selection rules listed in Section I are satisfied, the dipole term is present and normally is very large in comparison with all other terms. Thus for the first member of a spectral series in the visible or near ultraviolet where both general selection rules (transition is between odd and even terms and $\Delta J=0;\ \pm 1$) and special Russell-Saunders selection rules ($\Delta S=0$, $\Delta L=0,\ \pm 1$) are satisfied this dipole term has a value of the order of 10^8 sec.$^{-1}$. For higher members of a spectral series it may have values from 10^8 sec.$^{-1}$ down to 10^3 sec.$^{-1}$. For intercombination lines or other lines which satisfy the general selection rules but which violate the special selection rules for Russell-Saunders coupling the dipole term is still present but is often very small, the size of the term depending on how far the actual atom departs from the rigorous Russell-Saunders coupling. Thus the $2s\,{}^1S-2p\,{}^3P_1$ transition in Be I, which approximates Russell-Saunders coupling

[1] Strictly speaking a term should be added to A which is dependent on the radiation density. (See discussion by R. C. Tolman, Phys. Rev. **23**, 698 (1924).) As in nearly all cases considered this term is small, it will be neglected.

[2] Rubinowicz and Blaton, Ergeb. d. exakt. Naturwiss. **11**, 176 (1932).

[3] Condon and Shortley, *The Theory of Atomic Spectra*, (Cambridge University Press, 1935).

very closely, has a dipole transition probability of only 0.2 sec.$^{-1}$. On the other hand the corresponding $6s^1S-6p^3P_1$ line in Hg I which departs largely from Russell-Saunders coupling has a transition probability of 10^7 sec.$^{-1}$.

In transitions which do not satisfy the general selection rules, however, the electric dipole term vanishes completely regardless of the type of coupling present in the atom. It is thus seen that the empirically determined selection rules correspond to the theoretical rules for the presence of an electric dipole term in the transition probability. In the discussions in the remainder of the paper the terms permitted and forbidden will, unless otherwise explicitly stated, be used to denote the presence or absence of an electric dipole term in the transition probability of the line to which the terms refer.

If, on the other hand, the transition is between two odd terms or between two even terms, i.e., the first of the general selection rules for electric dipole radiation is violated, and if $\Delta J=0, \pm 1, \pm 2$ (the changes in J of $0\rightarrow 0$, $\frac{1}{2}\rightarrow\frac{1}{2}$, $0\rightleftarrows 1$ are excluded) the electric quadrupole radiation term is present. Likewise when the transition is between two odd or two even terms and $\Delta J=0, \pm 1$ ($0\rightarrow 0$ being excluded) the magnetic dipole term is present. In the case of Russell-Saunders coupling the electric quadrupole term is subject to the additional restrictions that $\Delta L=0, \pm 1, \pm 2$ ($L=0\rightarrow 0$ being excluded) and $\Delta S=0$ while for the magnetic dipole term it is necessary that $\Delta L=0$, $\Delta S=0$, $\Delta J=\pm 1$ and $\Delta n=0$ where n is the total quantum number of any electron. Thus intercombination quadrupole and magnetic dipole lines are excluded by these special selection rules. Even when all of these selection rules are satisfied, the values of these quadrupole and magnetic dipole terms are comparatively very small, usually ranging from 1 to 100 sec.$^{-1}$ for lines in the visible or near ultraviolet. In the case of lines satisfying the general conditions but violating the special Russell-Saunders conditions the value of this term of the transition probability may drop to values ranging from 1 to 10^{-5} sec.$^{-1}$.

The selection rules for both dipole and quadrupole radiation are violated by a few transitions, such for instance as a transition between an even and an odd term in which J changes by more than 1. In these cases the first term of the series representing the transition probability corresponds to octopole or even higher multipole radiation. Huff and Houston[4] and Brinkman[5] have discussed briefly the selection rules for octopole radiation and find the conditions necessary for the presence of this term are that the transition must be between odd and even terms and $\Delta J=0, \pm 1, \pm 2, \pm 3$. ($0\rightarrow 0$, $\frac{1}{2}\rightarrow\frac{1}{2}$, $1\rightarrow 1$, $\frac{1}{2}\rightleftarrows 1\frac{1}{2}$, $0\rightleftarrows 1$, $0\rightleftarrows 2$ being excluded for the electric octopole radiation). The normal value of the octopole term however is very small, being of the order of 10^{-6} of the size of a quadrupole term or 10^{-12} of a dipole term.

This octopole transition probability is so small that lines of this type would not be expected to appear under any circumstances. In the few cases where they have been observed the appearance is probably due not to the octopole radiation but to a minute dipole or quadrupole radiation term induced by some perturbation. Thus the theory on which the above discussion is based assumes that the nucleus is a point charge and that the atom is in a field-free space. In many atoms however the nucleus is a magnetic dipole[4] as well as an electric charge. Also in practically every source the atom is subject to external fields[2] either directly imposed or caused by nearby ions or even by atoms or molecules with a dipole moment. Perturbations of this type are also the cause of the appearance of certain lines whose transition probability according to this theory is absolutely zero, i.e., which are forbidden for all terms of the transition probability series. Such a case is the $6s^1S_0-6p^3P_0$ line of Hg.

From the above discussion it is therefore evident that very few transitions are absolutely forbidden, i.e., have a zero transition probability. In any actual sources the atoms, in which even these few exceptions occur, are subject to perturbations which remove the prohibition. The difference between lines that are permitted and that are forbidden by the empirical selection rules is therefore not an absolute difference. The rules merely distinguish between the lines with a very high transition probability (10^8-10^9 sec.$^{-1}$) and the lines with a very low probability (10^2 or less).

[4] L. D. Huff and W. V. Houston, Phys. Rev. **36**, 842 (1930).
[5] H. C. Brinkman, Dissertation, Utrecht, 1932.

This therefore explains why it is possible for forbidden lines to be observed occasionally.

IV. Quadrupole Radiation

Since most of the theory of spectra has been developed for permitted lines it has been based on the properties of electric dipole radiation. The theory of the behavior of the forbidden lines has had therefore to be redeveloped using the properties of electric quadrupole radiation, magnetic dipole radiation and in some cases higher multipole radiation as a basis. The development of this quadrupole radiation theory has been made largely by Rubinowicz although, as will be indicated in the following sections, certain details have been filled in by other investigators. The theory as developed up to 1932 was summarized by Rubinowicz and Blaton.[2] More recently Condon and Shortley[3] have also collected the important derivations. The results of these theoretical studies are as follows.

A. Selection rules, transition probabilities and line intensities

The selection rules and the orders of magnitude of the transition probabilities have been indicated in the preceding section. Exact values for the transition probabilities in hydrogen-like atoms have been worked out by Rubinowicz[6] and by Blaton.[7] For hydrogen these quadrupole transition probabilities are of the order of 10^{-5} of the dipole transition probability of permitted lines of approximately the same wave-length. Thus the quadrupole lines $1s^2S-3d^2D$ have transition probabilities of about 600 sec.$^{-1}$ while the adjacent dipole lines $1s^2S-3p^2P$ have values of about 1.6×10^8 sec.$^{-1}$. For higher series members the ratio of dipole to quadrupole transition probability is slightly decreased. Due to the very close proximity of the dipole and quadrupole lines in hydrogen none of these quadrupole lines have been observed. For corresponding lines in atoms of atomic number, Z, the transition probabilities of the quadrupole lines vary as Z^6 while those of the dipole lines vary as Z^4. Consequently in the x-ray spectra of heavy atoms, which may be considered as having approximately hydrogen-like structures, the transition probability of the quadrupole lines may reach as much as 2 or 3×10^{-2} of that of the dipole lines. This explains the rather more frequent occurrence of forbidden lines in x-ray spectra than in optical spectra.

Stevenson[8] has calculated the ratio of the absorption intensities of the first term of the forbidden s^2S-d^2D series to the first term of the s^2S-p^2P series in the spectra of various alkalis. When expressed in terms of the relative transition probabilities these yield the values shown in Table I. These relative transition probabilities

Table I. *Relative transition probabilities of permitted and forbidden lines* $A(s^2S-d^2D)/A(s^2S-p^2P)$.

	Na	K	Rb	Cs
Calc.	3.5×10^{-6}	2.5×10^{-6}	2.9×10^{-6}	
Obs.	1.1×10^{-6}	1.5×10^{-6}	2.7×10^{-6}	0.6×10^{-6}

have been determined experimentally by Prokofjew[9] using an anomalous dispersion method. His observations when corrected by Blaton[10] for the difference between the anomalous dispersion formulae for dipole and quadrupole radiation yield the values given in the lower row of Table I.

Calculations of the transition probabilities of the forbidden lines of C I, N II, O I, O II, O III and S II, which are important features of the spectra of the nebulae, have been made by Bartlett,[11] Stevenson[12] and Condon.[13] Condon's values which are the most recent and complete will be given in connection with the general discussion of the forbidden lines of these atoms in Section VII. It will there also be shown that the behavior of these lines in various astronomical objects is in qualitative agreement with that predicted from the calculated transition probabilities.

The general formulae for relative intensities of the lines in forbidden multiplets have been calculated by Rubinowicz[14] assuming electric quadrupole radiation and Russell-Saunders coupling. As in the case of the similar dipole formulae the calculations are based on the assumption that

[6] A. Rubinowicz, Physik. Zeits. **29**, 817 (1928).
[7] J. Blaton, Zeits. f. Physik **61**, 263 (1930).

[8] A. F. Stevenson, Proc. Roy. Soc. **A128**, 591 (1930).
[9] W. Prokofjew, Zeits. f. Physik **57**, 387 (1929).
[10] J. Blaton, Zeits. f. Physik **74**, 418 (1932).
[11] J. H. Bartlett, Phys. Rev. **34**, 1247 (1929).
[12] A. F. Stevenson, Proc. Roy. Soc. **A137**, 298 (1932).
[13] E. U. Condon, Astrophys. J. **79**, 217 (1934).
[14] A. Rubinowicz, Zeits. f. Physik **65**, 662 (1930). Formulae are also given in references 2 and 3.

the upper levels are so close together that the numbers of atoms arriving in each of them are proportional to the statistical weights $(2J+1)$ of the level. These intensities are subject to the usual dipole sum rule which states that the sum of the intensities of the lines from a given initial (or to a given final) level is proportional to the statistical weight $(2J+1)$ of the given initial (or final) level. However, because of the possibility of a change in ΔJ of ± 2, more lines appear in quadrupole than in the corresponding dipole multiplet and the intensities are therefore quite different than in the dipole case.

Since these formulae do not apply to intercombination lines the number of cases where an observational check can be obtained is very limited. Prokofjew's[10] observation of the $s\,^2S-d\,^2D$ multiplet in some of the alkalis gave approximately the theoretical 3 to 2 ratio for the two components. The only other multiplets of this type that have been observed with any completeness are the $3d^64s\ ^6D-3d^54s^2\ ^6S$ and $3d^7\ ^4F-3d^6\ 4s\ ^4G$ multiplets of Fe II that were found by Merrill in the spectrum of η Carinae. As will be seen in Table X in Section VII the observed intensities agree as well as could be expected with the theoretical values.

B. Absorption and anomalous dispersion

Tolman[15] has given the relationship between the absorption coefficient of a line and its transition probability (Eq. (3)). Since the formula is derived purely from thermodynamic reasoning it applies to quadrupole as well as dipole radiation.

$$A_{21}=8\pi\nu^2 p_1/cN_1p_2\int_0^\infty \alpha d\nu. \tag{3}$$

A_{21} is the transition probability for a transition from state 2 to state 1. p_1 and p_2 are the statistical weights of the two states. N_1 is the number of atoms in state 1 per unit volume of the absorbing gas. α is the absorption coefficient for light of frequency ν. From Eq. (3) it is seen that the integral of α across a spectrum line is proportional to the transition probability. Furthermore for the same value of N_1 and for a given range of the spectrum the proportionality constant is of the same order of magnitude for all lines since p_1 and p_2 are small integers that can differ at most by 2 in the case of dipole radiation and by 4 in the case of quadrupole radiation. It is therefore evident that the absorption coefficient of quadrupole lines is 10^{-6} to 10^{-10} of that of the electron dipole or permitted lines. Consequently the quadrupole lines are very rarely observed in absorption and then only under conditions of high density and long absorbing path.

As mentioned above the formulae for the anomalous dispersion in the neighborhood of a quadrupole line has been worked out by Blaton.[10] According to this formula, if μ is the index of refraction, the value of $\mu-1$ is four times as great near a quadrupole line as at the same distance from a dipole line, having the same transition probability, frequency, etc.

C. Zeeman effect

The splitting up of the levels of an atom into their component states by the presence of a magnetic field is, of course, independent of the types of transitions that may occur between the states. Consequently the Landé theory of the position of the components of a level in a magnetic field applies to forbidden as well as permitted lines.

The selection, polarization and intensity rules for the Zeeman components of a spectrum line are different for various kinds of radiation, however. These rules for electric quadrupole radiation and weak fields have been calculated in detail by Rubinowicz and summarized by Rubinowicz and Blaton.[2] Milianczuk[16] has derived similar formulae for field strengths between the weak field and Paschen-Back cases. Blaton[17] has given the selection and polarization rules for magnetic dipole radiation and Huff and Houston[4] for the complete octopole radiation. Table II summarizes these selection and polarization rules in comparison with the corresponding electric dipole rules. From the table it is evident that the longitudinal Zeeman effect, $(\alpha=\pi/2)$ i.e., when the source is viewed along a direction parallel with the field, is the same for all types of radiation. For the transverse effect $(\alpha=0)$ however, the Zeeman patterns of the various types of

[15] R. C. Tolman, Phys. Rev. **23**, 700 (1924).

[16] B. Milianczuk, Zeits. f. Physik **74**, 825 (1932).

[17] Blaton, Zeits. f. Physik **89**, 155 (1934).

TABLE II. *Polarization and selection rules for Zeeman patterns.* π = plane polarized parallel to field; σ = plane polarized perpendicular to field; el = elliptically polarized; cir = circularly polarized; r = right; l = left; Δm = change in magnetic quantum number.

ELECTRIC DIPOLE Δm	$\alpha=0$	$\pi/2$	ELECTRIC QUADRUPOLE Δm	$\alpha=0$	$\pi/4$	$\pi/2$	COMPLETE OCTOPOLE Δm	$\alpha=0$	$\pi/2$
+1	σ	r cir	+2	σ	r el	—	+3	σ	—
0	π	—	+1	π	σ	r cir	+2	π	—
−1	σ	l cir	0	–	π	—	+1	σ	r cir
			−1	π	σ	l cir	0	π	—
MAGNETIC DIPOLE			−2	σ	l el	—	−1	σ	l cir
	$\alpha=0$	$\pi/2$					−2	π	—
							−3	σ	—
+1	π	r cir							
0	σ	—							
−1	π	l cir							

radiation differ radically since no two types of radiation have the same selection and polarization rules. Observations in this direction provide then a conclusive test for the type of radiation that a given spectrum line represents.

The first observations of the Zeeman effect of a quadrupole line were made by McLennan, McLeod and Ruedy[18] on the $p^4\,{}^1D - p^4\,{}^1S$ line of O I. As they observed only in the longitudinal direction, however, the pattern did not differ from that of a dipole line. Two years later, however, Frerichs and Campbell[19] observed this same line in the transverse direction and found all of the additional components predicted for quadrupole radiation. Still more recently Segrè and Bakker[20] have made very extensive studies of the Zeeman patterns of the $s^2S - d^2D$ lines of Na and K. They observed both the transverse effect and at $\alpha = \pi/4$. In the case of Na the separation of the ${}^2D$ term is so small that all observed fields gave essentially the Paschen-Back effect. In K however the separation was large enough so that the pattern could be studied under conditions corresponding to both the weak field case of Rubinowicz and the intermediate case of Milianczuk. In all cases the theory was completely confirmed. Niewodniczanski[21] has observed the transverse Zeeman pattern of the magnetic dipole line (${}^3P_1 - {}^1S$) in Pb with results in agreement with the theoretical predictions.

[18] J. C. McLennan, J. H. McLeod and R. Ruedy, Phil. Mag. **6**, 558 (1928).

[19] Frerichs and Campbell, Phys. Rev. **36**, 151, 1460 (1930).

[20] E. Segrè, Zeits. f. Physik **66**, 827 (1930). E. Segrè and C. J. Bakker, Zeits. f. Physik **72**, 724 (1931).

[21] H. Niewodniczanski, Acta Physica Polonica **3**, 285 (1934).

V. INTENSITIES OF FORBIDDEN LINES

From Eq. (1) it is evident that, by neglecting the effects of self-absorption, the intensities of all lines corresponding to transitions from the same upper level are proportional to the transition probabilities of the lines. Furthermore the above sections have shown that the transition probability of a forbidden line is of the order of 10^{-6} of that of a permitted line of the same type and spectral range. Consequently in cases where an atom may leave a given upper state by both permitted and forbidden transitions it is evident that the intensity of the forbidden line will be so small in comparison with that of the permitted line that in general it will be below the threshold intensity necessary to record on the photographic plate or to be seen by the eye. The idea that lines of this type are forbidden is therefore for practical purposes correct.

Except in extreme cases where the transition probabilities may be changed by the presence of a very large electric or magnetic field the relative intensity of two lines from the same upper state is independent of the physical conditions of excitation. Consequently under no conditions can quadrupole or forbidden lines become relatively strong or play an appreciable role in any excitation process in comparison with permitted lines having the same upper level. For this reason the remaining part of the paper will be confined to the discussion of forbidden transitions from metastable states, i.e., states from which no permitted or electric dipole radiation is possible.

In the case of transitions from metastable states all of the transition probability or A terms in the denominator of the intensity Eq. (1) are very small having a value of at most 10^2 sec.$^{-1}$ and in many cases very much smaller. It is therefore necessary to consider the value of B the probability of removal by collision and of C the probability of removal by absorption as either of these may be very large in comparison with the A terms.

A. Removal from the metastable state by collisions

According to kinetic theory a given atom in air under standard condition has of the order of 10^{10} collisions per second. At lower pressures the number decreases proportionately with the pressure reaching 10^4 collisions per second at about 10^{-3} mm which is the lowest pressure at which a glow discharge can be maintained in a Geissler tube of feasible size. However the probability that a collision of the type considered by the kinetic theory will result in the removal of the atom from the metastable state is often far from unity. In other words the collisional cross section for a collision of either the first or the second kind may differ widely from the cross section for an ordinary kinetic theory collision.

A very large number of experiments have been performed to determine the effect of collisions on atoms in excited states. The results of these experiments have been collected and summarized by Mitchell and Zemansky.[22] Unfortunately these experiments have yielded very few quantitative measures of the collisional cross sections for collisions of either the first or second kind from which values of C the probability of the occurrence of these types of collision can be calculated. Indeed such evidence as is available indicates that the collisional cross section is a rapidly varying function of the relative velocity and the structures of the colliding particles.

While definite quantitative information is lacking, the following qualitative properties seem to be suggested by these and other experiments.

Electron-atom collisions. In this case the only appreciable transfers of energy that can occur are between the kinetic energy of the electron and potential energy of the atom. For a collision of the first kind, i.e., one in which kinetic energy is transferred to potential, the available evidence[23] indicates that the collisional cross section is very large when the kinetic energy of the electron is only slightly above that necessary to raise the atom to an excited state and the electron is therefore able to give up practically all of its kinetic energy. For electron energies higher than this the collisional cross section falls off rapidly. By the principle of microscopic reversibility a large collisional cross section should be expected for the reverse process in which a low velocity electron collides with an excited atom and takes up its potential energy in a collision of the second kind. Likewise this collisional cross section should fall off rapidly as the velocity of the impinging electron increases.

Atom-atom collisions. Two main types of energy transfer are of interest. In the first type kinetic energy of the colliding atoms is transferred to potential energy of one of the atoms or *vice versa.* The very meager experimental evidence available indicates that the collisional cross section for this type of transfer is small particularly when the kinetic energy of the impinging particles is of the same order of magnitude as the potential energy of the excited state in the atom.[24] Likewise the probability of a collision of the second kind in which all of the potential energy of an excited state is transferred to kinetic energy of the atoms taking part in the collision must also be very small by the principle of microscopic reversibility.

The second type of atom-atom collision is one in which the potential energy of an excited state in one atom is transferred to the other atom, taking part in the collision, thereby raising it to an excited state. Any difference in the potential energies of the two excited states is obtained from, or given to, the kinetic energies of the two atoms. The probability of this type of collision of the second kind is very large when the potential energies of the states in the two atoms are nearly equal, i.e., when very little energy is transferred to or from kinetic energy. As the difference in energy between the two states increases the collisional cross section falls off rapidly. These relationships have been predicted from theory. Experimentally also Beutler and Josephy[25] found that when Hg atoms excited to the $6p^3P_1$ state were mixed with sodium vapor the sodium lines that were most strongly excited were those starting from the 9^2S state which has very nearly the same energy of excitation as the 6^3P_1 state of Hg. Because of the very large number of energy states possessed by most molecules it is usually possible to find an excited state that closely

[22] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press), pp. 56–90, 236–255.

[23] See for example, O. Thieme, Zeits. f. Physik **78**, 412 (1932); W. C. Michels, Phys. Rev. **38**, 712 (1931), and references given by them.

[24] W. Maurer, Zeits. f. Physik **96**, 489 (1935).

[25] H. Beutler and B. Josephy, Zeits. f. Physik **53**, 747 (1929).

matches in energy that of the excited state of any other atom with the result that molecules are particularly effective in collisions of the second kind of this type. Likewise the still more complicated structure possessed by a solid makes it practically certain that a collision between an excited atom and a solid will result in the de-excitation of the atom.

These general considerations show at once that, under most laboratory conditions of excitation, the value of B, the probability of removal from a metastable state by a collision, usually of the second kind, is very large compared to the probability, A, of spontaneous transition with the emission of a forbidden line. Consequently from Eq. (1), it is evident that the intensity of such a line is ordinarily so small that for practical purposes it may be considered as forbidden.

These collision probabilities also give the reasons for the methods which have been found most effective in bringing out the few forbidden transitions that have been observed in the laboratory. Thus in the classical experiments of McLennan, McLeod and McQuarrie[26] on the laboratory production of the auroral line of O I it was found that with pure oxygen a pressure of about 2 mm was most effective. At higher pressures the intensity was presumably decreased by collisions of the second kind with oxygen molecules. At lower pressures the atoms in the metastable state diffused rapidly to the walls of the discharge tube where they were removed from the metastable state by a collision of the second kind with the wall. The highest intensity of the auroral line was found in a mixture of a small amount of oxygen in a much larger amount of a noble gas. Since the noble gas atoms have no excited states below 10 to 20 electron volts they are incapable of taking up any potential energy from the metastable oxygen atom whose available energy is but 5.3 electron volts. As collisions in which all of the energy is transferred to kinetic energy have a very low probability the presence of the noble gases even at relatively high pressures does not therefore appreciably increase the number of collisions of the second kind in the gas itself. On the other hand the presence of the noble gas does prevent diffusion to the walls of the excited oxygen atoms and their resultant de-excitation there.

The fact that very little success has been attained in the excitation of the forbidden lines of highly ionized atoms is probably due to the high probability of collisions of the second kind with low velocity electrons that are always present in great numbers in sources where highly ionized atoms are found.

B. Removal from the metastable state by absorption of radiation

The probability, C, of the removal of the atom from the metastable state by the absorption of a permitted line corresponding to a transition ending in the state, is proportional to the density of radiation of the wave-length that the excited atom can absorb. As was first pointed out by Eddington[27] this high value of C is an important factor in preventing the emission of forbidden lines with any appreciable intensity in the atmospheres of many stars. Thus in the atmosphere of the sun the radiation density is such that a Ca^+ atom is removed from the normal $4s^2\ {}^1S$ state about 2×10^4 times per second by absorption of the H and K lines. A similar value of C would be expected for any stable or metastable state, permitted transitions to which fall in the neighborhood of the maximum of the solar radiation near 5000A. Thus even in the case of the forbidden lines of Fe II, whose transition probabilities A are relatively high for quadrupole radiation, the intensity in the flash spectrum is cut down by a factor of several thousand.[28] This decrease in intensity is due almost entirely to the large value of C rather than to the value B of the collision probability since it is estimated that in the chromosphere the pressure is so low that even ordinary kinetic collisions occur only about once per second.

On the other hand most of the atoms of the first two rows of the periodic table and of the higher stages of ionization of the atoms of the first long period have metastable states, the only permitted transitions to which fall in the extreme

[26] J. C. McLennan, J. H. McLeod and W. C. McQuarrie, Proc. Roy. Soc. **A114**, 1 (1927).

[27] H. S. Eddington, M.N.R.A.S. **88**, 134 (1927).

[28] I. S. Bowen and D. H. Menzel, Pub. A. S. P. **40**, 332 (1928).

ultraviolet. In the case of a relatively cool star such as the sun the radiation density in this region of the spectrum is very much smaller than in the visible and therefore the value of C may be so small as to allow the appearance of the forbidden lines of these atoms with a high intensity.

It is therefore evident that the sources which have the physical conditions under which even the forbidden transitions from metastable states can appear with strengths comparable to those of the permitted lines are very rare. The optimum laboratory conditions for bringing out even faintly a few of these lines have already been discussed. Among astronomical objects the great majority of stars can be eliminated as sources since they emit an absorption spectrum and forbidden lines do not have an appreciable absorption coefficient. Also many of the small group of stars with an emission spectrum do not possess the necessary conditions of low density of both matter and radiation. The conditions for the appearance of forbidden lines in their full strength, which is reached when the number of transitions equals the number of atoms arriving in the metastable state, are most completely fulfilled in the nebulae and are approximated in the later stages of a nova and in a few stars with very extensive atmospheres. As the very great strength of the forbidden lines in these objects is caused to a large extent by their rather special mechanism of excitation the conditions of this excitation will be discussed in detail in the next section.

VI. Physical Conditions and Mechanism of Excitation in the Nebulae

The density in the nebulae is usually estimated to be of the order of 10^{-18} g per cc or less. Assuming that the density is 10^{-18} g per cc, that the temperature is 10,000°C and that there is one free electron for each atom, one finds according to the kinetic theory that the mean time between the collisions of a given atom is of the order of a minute. The density of radiation is also very low. Even in the compact planetary nebulae the radiation is only 10^{-6} to 10^{-8} as intense as at the sun's surface.

Because of the low density of the nebulae they cannot contain within themselves the source of the energy which they radiate but must receive their energy from some outside source, presumably a nearby star. Such a connection with a star was first suggested by Sir William Herschel.[29] The idea was not generally accepted however until Hubble[30] summarized the evidence found in a large number of observations by V. M. Slipher, W. H. Wright, H. D. Curtis and himself. Thus Hubble found that nebulae associated with stars cooler than B I have an absorption spectrum of the same class as that of the star and have the surface brightness that might be expected if star light were reflected or scattered by the nebula. Nebulae having an emission type spectrum, and therefore of the kind that concerns us here, are always associated with stars hotter than B I. Since these hot stars are just those that emit a large amount of energy in the extreme ultraviolet, Menzel[31] and Zanstra[32] independently suggested that absorption of this extreme ultraviolet was the source of excitation of the emission spectrum of these objects.

The only mechanism by which the atoms of the nebulae can take up an appreciable amount of this extreme ultraviolet radiation is that of photoelectric absorption of light of a wave-length less than that of the series limit of the atom. Such an absorption ionizes the atom which at some later time recombines with an electron and emits its characteristic spectrum. For any particular atom there is a definite relationship between the number of quanta of ultraviolet light absorbed and the number of quanta emitted in the observable range. Thus in the case of hydrogen Zanstra was able to show that the number of quanta of radiation in the lines of the Balmer series, all of which are in the observable range, is equal to the number of ultraviolet quanta absorbed. A measurement of the observable radiations of a given atom excited in the nebula surrounding the star can therefore be used to determine the amount of the stars extreme ultraviolet radiation having a wave-length less than

[29] Sir William Herschel, Abridged Phil. Trans. **17**, 25 (1791).
[30] E. Hubble, Astrophys. J. **56**, 162, 400 (1922).
[31] D. H. Menzel, Pub. A. S. P. **38**, 295 (1926).
[32] H. Zanstra, Astrophys. J. **65**, 50 (1927); Zeits. f. Astrophys. **2**, 1 (1931).

the series limit of that atom. By assuming the Planck black body radiation law it is then possible to determine the temperature of the exciting star by comparing the amount of the extreme ultraviolet radiation determined in this way with the amount of the star's radiation in the directly observable range of the spectrum. Using the lines of H and He which are strong in most nebulae Zanstra found temperatures which were in very satisfactory agreement with those obtained by other methods. This furnishes strong confirmation of the correctness of this mechanism of excitation of the lines of H and He.

Except for these lines of H and He however the nebular spectra contains no strong lines whose excitation can be attributed to this primary mechanism. The few strong permitted lines of O III and N III that are observed in several nebulae are just the lines of these ions that can be excited by a secondary mechanism even though these ions are of very low abundance. The absence of the complete spectra of these ions therefore indicates that these ions are so rare that their spectra are not excited with any strength by the primary mechanism.[33] H I (series limit 912A, ionization potential, 13.5 electron volts, He I (series limit 504A, I. P. 24.5 ev) and He II (series limit 228A, I. P. 54.1 ev) are therefore by far the most abundant constituents of the nebulae.

The absorption coefficient for photoelectric absorption is greatest at a wave-length just below the series limit and falls off rapidly as the wave-lengths of the absorbed light differs more and more from that of this limit. Consequently each one of the three abundant ions tends to absorb most of the ultraviolet radiation between its own series limit and that of the next ion. The energy of the absorbed quantum in excess of that necessary to ionize the atom is carried away in the form of kinetic energy of the ejected electron. Consequently electrons ejected from H will possess energies of from 0 to $24.5-13.5=11$ electron volts, from He I of from 0 to 29.6 electron volts and from He II of from 0 up. Most of these electrons have energies of less than 10 electron volts and the few that start with higher energies are rapidly reduced to less than 10 electron volts by impact with slow electrons or by the excitation of the abundant H atoms. Additional low energy electrons are ejected from the H by the absorption of the secondary extreme ultraviolet lines emitted by He and He^+.

This means therefore that a very appreciable fraction of the energy taken up by the nebula from ultraviolet star light appears in the form of electrons with energies less than 10 electron volts.[34] Since the lowest excitation potential of any of the abundant H, He or He^+ atoms is 10 electron volts this energy cannot be taken up by these elements. It therefore must all be used for the excitation of such elements as have excited states with excitation potentials of less than 10 volts even though these elements may be rare in comparison with H and He. Furthermore this energy can only be used for the excitation of the lines of these elements that start from these states of low excitation potential. As will be pointed out later this rather special mechanism of excitation by low velocity electrons is the chief source of excitation of the forbidden lines in the nebulae and plays a very important role in determining the relative intensities of the forbidden lines and the permitted lines of the same elements and of the abundant H and He.

Assuming this mechanism, it is possible to obtain an independent determination of the amount of extreme ultraviolet radiation absorbed by the nebulae from the intensity of the lines of low excitation potential, i.e., the forbidden lines emitted by it. Zanstra has determined the temperature of the exciting stars by this method with results in agreement with those obtained in other ways.

The mechanisms discussed above are also the source of excitation of the emission spectra of the novae and of certain stars with very extensive atmospheres.

VII. Tables and Discussion of Forbidden Lines

Since certain astronomical objects are the only sources in which forbidden lines play any very large role, the only forbidden lines that are of great interest are those that fall in the astro-

[33] For more extensive discussion see I. S. Bowen, Astrophys. J. **81**, 1 (1935).

[34] I. S. Bowen, Astrophys. J. **67**, 1 (1928).

nomically observable range from 3000 to 10,000A. The following tables and discussion will therefore in general be limited to lines falling in this range. A very few extreme ultraviolet forbidden lines of the most abundant elements will also be noted since, because of their great intensity, these lines may play some role in the excitation of secondary radiations in the observable range.[35]

Since very few of the forbidden lines have ever been produced in the laboratory it is necessary to determine their wave-lengths from the differences of the term values of the initial and final states of the transitions involved. In general these term values can be determined only after a fairly complete analysis of the spectrum of the atom under consideration has been made. This is particularly true for the lighter elements since many of the forbidden lines involve transitions between singlet terms or between terms of different multiplicity, and since for these elements the singlet terms and intercombination lines, that are necessary to fix the relative position of terms of different multiplicity, are usually the last items found in any series analysis. In most of the cases, even when the analysis is complete, the necessary terms are fixed by the observed wave-lengths of extreme ultraviolet lines in the range from 300 to 1500A where most of the available measurements have been made on short focus instruments of rather low accuracy. Furthermore, since the error in wave number units varies as the square of the wave-length an error of 0.01A in this range introduces an error of 0.11 to 3A in the wave-length of a calculated line near 5000A.

Where the spectrum of an atom has not been analyzed completely enough to make possible a direct determination of the position of the forbidden line, approximate wave-lengths may often be obtained by extrapolation or interpolation from other atoms of the same structure. Thus to a first approximation the wave numbers of the corresponding forbidden lines of an isoelectronic sequence vary linearly with the atomic number in the majority of the atoms of interest. This progression is particularly regular for the atoms of the first two rows of the periodic table since the configurations in which the important metastable states occur are far away from the perturbing effects of other configurations.

The column marked error in the following tables indicates the maximum deviation from the predicted position that may be allowed for the lines of the multiplet indicated. In general errors of less than 10A arise from uncertainties in the wave-length determinations of the ultraviolet lines used to fix the terms. Errors greater than this indicate an extrapolated or interpolated value. The references on the calculated wave-lengths refer to the series analysis used in the calculation of the wave-lengths. References on the observed wave-lengths give the original identification of the observed nebular line as the transition indicated. In cases where the transition probability has been calculated by Condon its value, in reciprocal seconds, is listed in the row marked A. The excitation potentials of the various metastable states in electron volts are indicated in the second and third columns from the last. For comparison the lowest excitation potential of any permitted line that falls in the observable range from 3000 to 10,000A is included in the last column. Unless otherwise noted all observed nebular wave-lengths were measured by Wright.[36]

To illustrate the positions of the metastable states and the forbidden transitions from them in the structure of the atoms, energy diagrams of some of the more important ions have been included. Since for the problems under consideration the differentiation between odd and even terms is of primary importance the various terms of the ion have been arranged in columns corresponding to successive values of the arithmetical sums of the azimuthal quantum numbers (l) of the electrons in unfilled shells. When so arranged dipole or permitted lines correspond to jumps of one or in certain rare cases of three columns. Quadrupole or forbidden lines on the other hand correspond to jumps between terms in the same column or occasionally between terms two columns apart. Solid lines connecting terms indicate strong observed permitted lines while dotted lines represent forbidden transitions from metastable states. The scale at the side indicates the energy in electron volts.

[35] I. S. Bowen, Zeeman Verhandelingen (1935), p. 55.

[36] W. H. Wright, Pub. Lick Obs. **13**, 193 (1918); Lick Obs. Bull. **17**, 1 (1934). Pub. A. S. P. **46**, 92, 280 (1934).

The horizontal lines at the top of each diagram show the energy necessary to remove an electron from the ion and leave the next ion in the state listed. The term types of the important levels are shown by the usual symbols (^1S, ^3P, ^4D, etc.). The electron configuration of any level may be found by adding an electron in the orbit indicated to the electron configuration of the next ion having the same symbol as the level considered. In a few cases the complete configuration is listed directly.

One-electron systems H I, He II, etc. These atoms have one metastable state, namely, $2s^2S$. However as this state coincides with the $2p^2P_{\frac{1}{2}}$ state, any forbidden transition from the $2s^2S$ state will have exactly the same wave-length as the permitted transition from the $2p^2P_{\frac{1}{2}}$ state. Consequently no new lines can be expected under conditions favorable to forbidden lines.

Two-electron systems, He I, Li II, etc. The $1s2s^1S$ and $1s2s^3S$ states of these atoms are metastable. However the only possible forbidden transitions from these states are $1s^2\,{}^1S-1s2s^1S$ and $1s^2\,{}^1S-1s2s^3S$ which occur at 601.391A and at 625.459A, respectively, in He I and at still shorter wave-lengths in the heavier ions. While these He lines are in the extreme ultraviolet and cannot therefore be observed directly, they are doubtless very strong in the nebulae and may play some role in exciting observable radiation.[35]

Three-electron systems, Li I, Be II, B III, C IV, etc. These atoms have no metastable states.

Four-electron systems, Be I, B II, C III, N IV, O V, etc. In these atoms the $2s2p^3P_0$ and $2s2p^3P_2$ states are metastable. Because of the closeness with which these light atoms approximate Russell-Saunders coupling the only dipole transition from the $2s2p^3P_1$ state, namely $2s^2\,{}^1S-2s2p^3P_1$, has a very small transition probability. Thus the calculated value of this transition probability in Be I is only 0.2 sec.$^{-1}$ which is smaller than that of many forbidden lines. All of the $2s2p^3P$ states have therefore the characteristics of metastable states and the transitions from them to the $2s^2\,{}^1S$ state should behave like forbidden lines. None of these transitions have been observed and all of them fall outside of the astronomically observable range except those of Be I which should be located at 4548 ± 5A.

Five-electron systems, B I, C II, N III, O IV, etc. In these elements the only strictly metastable state is the $2p^2P_{1\frac{1}{2}}$ level. However this is so close to the stable $2p^2P_{\frac{1}{2}}$ level that any transitions between them fall in the far infrared. As in the preceding sequence the Russell-Saunders coupling is very closely approximated with the result that the lines of the $2s^22p^2P-2s2p^2\,{}^4P$ multiplet, which are the only possible transitions from the $2s2p^2\,{}^4P$ levels, behave as forbidden lines from metastable states. None of these lines have been observed in the laboratory, and all of them lie outside the astronomically observable range except those of B I which should fall at about 3300 ± 300A.

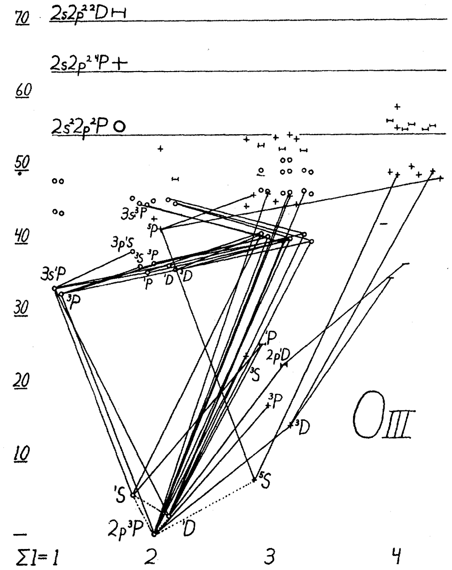


FIG. 1. Structure of a six-electron system.

Six-electron systems. Fig. 1 is an energy diagram of O III which is a typical ion of this group. As is at once evident the lowest configuration of these atoms is $2s^22p^2$ which gives rise to ^3P, ^1D and ^1S terms. Since all of these levels belong to an even configuration, transitions between them are forbidden and all of the levels except the lowest one $^3P_0$ are metastable.

Of the forbidden transitions between these levels those between the levels of the ^3P term are

TABLE III. *Six-electron systems.*

		$^3P_1-{}^1D$	$^3P_2-{}^1D$	$^1D-{}^1S$	$^3P_1-{}^1S$	Excitation Potentials ^1D	^1S	Permitted
C I	Calc.[37]	9822.9	9849.5±3	8727.4±3	4621.4±1	1.3	2.7	9
	A	0.00005	0.00015	1.0	0.0041			
N II	Calc.[37]	6548.4	6583.9±1	5755.0±1	3063.0±0.5	1.9	4.0	20
	Obs.	6548.1[34]	6583.6	5754.8[38]				
	A	0.00081	0.0024	1.7	0.066			
O III	Calc.[37]	4959.5	5007.6±2	4363.2±1		2.5	5.3	36
	Obs.[34]	4958.91	5006.84	4363.21				
	A	0.006	0.018	1.8	0.102			
F IV	Calc.[39]	3996.3	4059.3±3	3532.2±3		3.1	6.6	58
Ne V	Calc.[40]	3344	3424±20	2972±20		3.8		>86
	Obs.[41]	3345.8	3425.8					

[37] B. Edlén, Nova Acta Reg. Soc. Sci. Upsaliensis **9**, No. 6 (1934).
[38] F. Becker and W. Grotrian, Ergeb. d. exak. Naturwiss. **7**, 65 (1928).
[39] B. Edlén, Zeits. f. Physik **92**, 19 (1934).
[40] Extrapolated or interpolated values.
[41] P. Swings and B. Edlén, Comptes rendus **198**, 1748 (1934); I. S. Bowen, Pub. A. S. P. **46**, 145 (1934).

in the far infrared. Transition probabilities as calculated by Condon are equal to 0 for the $^3P_0-{}^1D$ and $^3P_0-{}^1S$ lines. The transition from ^1S to $^3P_2$ has a transition probability only about 0.001 as great as that of the transition to $^3P_1$. Consequently the intensity of the $^3P_2-{}^1S$ line is negligible in comparison with the $^3P_1-{}^1S$ line under all circumstances. The predicted and astronomically observed wave-lengths of the remaining transitions in these six electron ions are collected in Table III.

C I. The only line of C I in the range of the spectrum that has been investigated in the nebulae is $^3P_1-{}^1S$. However the transition probability of this line is only 1/240 of that of the infrared $^1D-{}^1S$ transition from the same level. This coupled with the known rarity of neutral atoms in the nebulae explains the failure of the line to be observed even though other evidence points to a relatively high abundance of carbon in these objects.[33]

N II. In N II the $^3P_1-{}^1D$, $^3P_2-{}^1D$, $^1D-{}^1S$ lines are quite accurately predicted from a complete analysis and are all found in a large number of nebulae. The $^3P_1-{}^1S$ line is not observed since its transition probability is only 1/25 of that of the $^1D-{}^1S$ transition from the same level and since it falls so near the limit of transmission of the atmosphere that its intensity is largely cut down by absorption. Attention should be called to the fact that the ^1D state has a relatively long lifetime of about $1/(0.00081+0.0024)=300$ sec. as compared to 0.6 sec. for the ^1S state.

O III. The metastable levels of this ion have been completely determined and all predicted lines have been observed in the nebulae. In most of the planetary nebulae the $^3P_1-{}^1D$ and $^3P_2-{}^1D$ lines at 4959 and 5007A are the strongest lines in the spectrum. The ^1D state again has a much longer life (42 sec.) than the ^1S state (0.5 sec.).

F IV. While the positions of the lines of F IV can be predicted accurately none of them have been observed in the nebulae.

Ne V. No analysis has been made of the Ne V spectrum. However the long sequence of isoelectronic elements from C I to F IV makes possible an extrapolation to the position of the Ne V forbidden lines with an uncertainty of less than 20A. Another type of extrapolation fixes the separation between the two lines of the $^3P-{}^1D$ multiplet with an error of less than 1A. These extrapolations point unambiguously to the pair of nebular lines at 3346 and 3426A. Confirmation of this identification is found in the fact that these lines appear only in the nebulae of highest excitation and that the monochromatic images of the nebulae of these wave-lengths are the smallest known.

All forbidden lines of Na VI and the more highly ionized atoms of this sequence fall outside the observable range.

Confirmation of the excitation potentials and transition probabilities listed in the table is given by the behavior of the forbidden lines in the nebulae and in the novae. Thus in conditions of extremely low density of radiation and of matter such as are found in the nebulae, the probability of removal of the atom from a metastable state by collision, B, or by absorption, C, is small compared to the sum of the transition probabilities, A, of the forbidden jumps from the metastable states. Therefore, practically all atoms arriving in any one of the metastable states remain undisturbed until they jump from the state with the emission of the corresponding forbidden lines. Under these conditions the sum of the intensities of all forbidden lines from any metastable state is proportional to the number N of atoms arriving in that state per unit time, and is independent of the lifetime of the state. Thus in six-electron systems the number of atoms arriving in the ^1D state is many times as great as those arriving in the ^1S state since the statistical weight of the ^1D state is 5 times as great as the ^1S state and since the excitation potential of ^1D is less than half of that of ^1S. The number arriving in ^1D is further increased by the fact that the majority of the atoms arriving in ^1S jump to ^1D. Therefore under these conditions of very low density the $^3P_1-{}^1D$ and $^3P_2-{}^1D$ lines should be much stronger than the $^1D-{}^1S$ or $^3P_1-{}^1S$ lines.

On the other hand under conditions of higher density where B plus C is large compared to the transition probabilities A of the forbidden lines, Eq. (1) gives for the intensities of any line the value

$$I = NA_1 h\nu/(C+B). \tag{3}$$

If we make the plausible assumption that C and B have the same order of magnitude for all metastable levels of a given atom, the intensities of the lines are proportional to N, the number arriving in the upper level per unit time multiplied by A_1 the transition probability of the line. Thus in N II the transition probability of $^1D-{}^1S$ is 700 times as great as that of $^3P_2-{}^1D$ which is the most probable transition from the ^1D level. In O III the corresponding ratio is 100. Consequently, while N, the rate atoms are arriving in the state, still remains much smaller for the ^1S level than for the ^1D level, the very much larger value of the A of the $^1D-{}^1S$ transition more than counterbalances this and leads one to expect that the $^1D-{}^1S$ line should be stronger than the $^3P-{}^1D$ lines under these conditions.

These considerations were first used by Grotrian[42] and later by Menzel and Payne[43] to explain the behavior of these forbidden lines in the novae. Thus as the gaseous shell of the novae expands its spectrum rapidly changes from a stellar absorption type to an emission type spectrum. When these emission lines first appear, however, the density is still too high for the appearance of any of the forbidden lines and therefore only permitted lines are found. As the expansion continues B and C decrease and the forbidden lines begin to appear. However as B and C are still large compared to the A's of the forbidden lines the strongest lines and therefore the first to appear are the $^1D-{}^1S$ lines, i.e., 5755 in N II and 4363 in O III. As the nebulous shell recedes still further from the star the conditions approach those of the nebulae where B and C are very small with the result that in these later stages as in the nebulae the $^3P-{}^1D$ lines become the strongest lines of these elements that are present.

Attention should be called to the low excitation potential of these forbidden lines in comparison with that of the permitted lines of the same ions. Thus in O III (see Fig. 1) the lines corresponding to the nearby horizontal transitions from a $3p$ to a $3s$ orbit have the lowest excitation potential of any lines in the astronomically observable range. This excitation potential (see Table III) is 36 electron volts in comparison with 2.5 and 5.3 electron volts, respectively, for the forbidden lines from ^1D and ^1S levels. This furnishes at once the reason for the very great difference in the intensities of the permitted and forbidden lines. Thus O III is so much rarer than H, He I or He II in the nebulae that the intensities of its permitted lines, which are excited by the primary mechanism, are so small that the lines are very seldom if ever observed.[33] On the other hand O III is usually the most abundant ion with lines whose excitation potentials are low enough to make use of the large amount of energy that is available in the form of ejected electrons with kinetic energies of 0 to 10 volts. Consequently

[42] W. Grotrian, Zeits. f. Physik **60**, 302 (1930); Zeits. f. Astrophys. **2**, 78 (1931).
[43] D. H. Menzel and C. H. Payne, Proc. Nat. Acad. Sci. **19**, 641 (1933).

the forbidden lines which have these low excitation potentials are often the strongest lines in the nebular spectrum.

The reason for the very high relative intensity of the forbidden lines may be stated in another way. Thus, as discussed above, under the condition of extreme low density the intensity of any line depends solely on the number of atoms reaching the upper state. Under these conditions, therefore, the ${}^3P-{}^1D$ lines are (as far as the observable range is concerned) the true resonance lines of O III. Furthermore every one is familiar with the way in which the resonance D lines of sodium dominate the visible spectrum of that element when excited by relatively low energy electrons, such as one finds in a flame or furnace. If one considers then that other lines of Na in the visible range of Na have excitation potentials of less than twice that of the D lines while the permitted lines of O III have excitation potentials of over 14 times that of the forbidden ${}^3P-{}^1D$ lines it is not difficult to understand the great predominance of these forbidden lines in nebular spectra.

In addition to these metastable states the six electron atoms have one other state $2s2p^3\,{}^5S$, which behaves as a metastable state since the only transitions from it are intercombination lines having very low transition probabilities. Since the transition probabilities of the jumps from this level to $2s^22p^2\,{}^3P$ levels are probably much greater than of those to the $2s^22p^2\,{}^1D$ or ${}^1S$ levels, the $2s^22p^2\,{}^3P-2s2p^3\,{}^5S$ lines are the only transitions that have any appreciable intensity even under nebular conditions. However in all cases except possibly C I this transition falls outside of the observable range.

Seven-electron systems. The energy diagram of a representative atom of this type (O II) is shown in Fig. 2. The only metastable levels belong to the ${}^2P$ and ${}^2D$ terms of the low s^2p^3 configuration while the stable level is the ${}^4S$ term of the same configuration. Table IV lists the predicted and observed positions of the forbidden transitions between these levels. All of the ions of this sequence have been rather completely analyzed. The chief uncertainty in the predictions arises from the fact that the multiplet separations of the ${}^2P$ and ${}^2D$ terms are so small that the extreme ultraviolet multiplets involving these levels have not been completely resolved in several cases. This makes the exact structure of the forbidden multiplets quite uncertain in the case of Ne IV and Al VII in particular.

N I. None of the forbidden lines of this element have been observed in the nebulae although the ${}^4S-{}^2D$ line may have appeared in Nova Geminorum.[42] This is doubtless due to the rarity of neutral nitrogen in the objects where the conditions are conducive to the appearance of forbidden lines.

O II. All of the predicted lines of O II in the observable range have been found in the nebulae although the four line multiplet in the extreme

TABLE IV. *Seven-electron systems.*

		${}^4S-{}^2D_{1\frac12}$	${}^4S-{}^2D_{2\frac12}$	${}^4S-{}^2P_{\frac12}$	${}^4S-{}^2P_{1\frac12}$	${}^2D_{2\frac12}-{}^2P_{\frac12}$	${}^2D_{2\frac12}-{}^2P_{1\frac12}$	${}^2D_{1\frac12}-{}^2P_{\frac12}$	${}^2D_{1\frac12}-{}^2P_{1\frac12}$	Excitation Potentials ${}^2D$	${}^2P$	Permitted
N I	Calc.[44]	5198.5	5200.7±1	3466.4±0.5						2.4	3.6	12
O II	Calc.[37]	3726.2	3729.1±1			7318.6	7319.4	7329.9	7330.7±2	3.3	5.0	25
	Obs.[34]	3726.16	3728.91			7319.9[45]		7330.4				
	A	0.0000242	0.000037	0.049	0.041	1.0	2.3	3.3	1.7			
F III	Calc.[46]	2930.0	2933.1±3			5721.2		5733.0±4		4.2	6.4	43
Ne IV	Calc.[47]					4713.0	4715.2	4718.6	4720.8±8	5.1	7.7	>66
	Obs.[48]								4725.5?			
Na V	Calc.[49]					4011.2	4015.3	4017.5	4021.6±4		9.0	>92
Mg VI	Calc.[49]					3485.5	3488.1	3500.4	3503.0±4		10.3	>121
Al VII	Calc.[49]					3068.8	3074.0	3093.4	3098.7±8		11.7	>153

[44] E. Ekefors, Zeits. f. Physik **63**, 437 (1930).
[45] Measurements by Merrill, Pub. A. S. P. **40**, 254 (1928).
[46] B. Edlén, Zeits. f. Physik **93**, 433 (1935).
[47] J. C. Boyce, Phys. Rev. **46**, 378 (1934).
[48] J. C. Boyce, D. H. Menzel and C. H. Payne, Proc. Nat. Acad. Sci. **19**, 581 (1933).
[49] J. Soderquist, Nova Acta Reg. Soc. Sci. Upsaliensis **9**, No. 7 (1934).

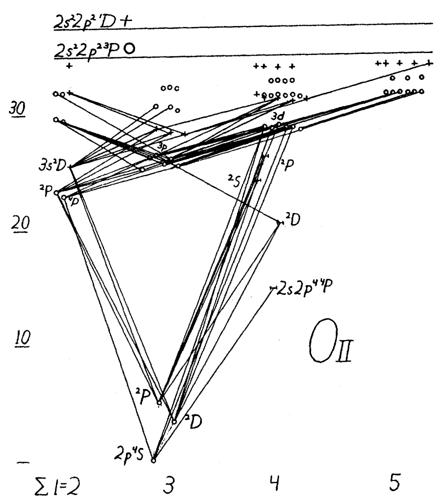


FIG. 2. Structure of a seven-electron system.

red has been only partially resolved. Attention should be called to the very long mean lives of 12 and 8 hours of the $^2D_{1\frac{1}{2}}$ and the $^2D_{2\frac{1}{2}}$ states, respectively. In comparison the life times of the ^2P states are only about 1/4 second.

F III. Only one forbidden multiplet is predicted in the observable range for F III and the remaining ions of this sequence. The lines of this multiplet should never be very strong since in each case the lines start from the ^2P term which has the higher excitation potential of the metastable terms of these ions. A very strong wide line in Nova Pictoris is near the predicted position of this F III multiplet and very faint lines are found in one or two nebulae near this wave-length. However as pointed out by Edlén and Swings[50] these correlations are very doubtful because of the absence from these objects of the lines of F II and F IV, some of whose excitation potentials are less than half as great.

Ne IV. Several faint nebular lines fall near the predicted position of this multiplet in Ne IV and can probably be attributed to it. However, higher resolution of the extreme ultraviolet lines used in the Ne IV analysis and more complete nebular observations are necessary before an exact correlation between the observed lines and the individual components of the predicted multiplet can be made.

Na V, Mg VI, Al VII. Because of both the high stage of ionization that these lines represent and their high excitation potentials none of the lines of these ions could be expected to appear with any reasonable concentration of Na, Mg or Al.

As in the preceding sequence the observable permitted lines that have the lowest excitation potential are those corresponding to an electron jump from a $3p$ to a $3s$ orbit. However it is seen from Table IV that their excitation potential is very much higher than that of the forbidden lines and this again furnishes the explanation for the great relative intensities of the latter lines. Likewise there are in this sequence high level meta-

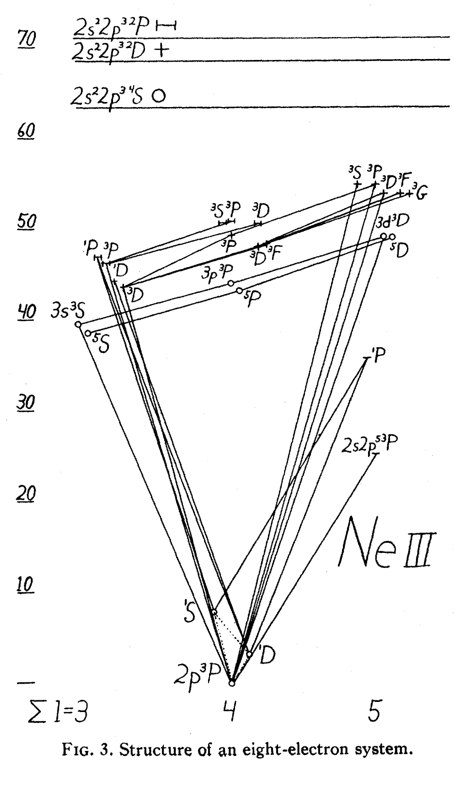


FIG. 3. Structure of an eight-electron system.

[50] Edlén and Swings, Comptes rendus **198**, 1842 (1934).

TABLE V. *Eight-electron systems.*

		$^3P_1-{}^1D$	$^3P_2-{}^1D$	$^1D-{}^1S$	$^3P_1-{}^1S$	Excitation Potential ^1D	^1S	Permitted
O I	Lab.	6363.88[51]	6300.23±0.2	5577.341±0.02[52]	2972.31±0.05	2.0	4.2	11
	Obs.	6364[53]	6302	5577[54, 55]				
	A	0.0025	0.0075	2.0	0.18			
F II	Calc.[46]	4869.2	4789.5±2	4157.5±2		2.6	5.5	26
Ne III	Calc.	4000[40]	3900±50	3342.8±2[47]		3.2	6.9	>44
	Obs.	3967.51[48]	3868.74	3342[55]				
Na IV	Calc.	3366[40]	3245±30			3.8		>66

[51] J. J. Hopfield, Phys. Rev. **37**, 160 (1931) (Direct observation).
[52] J. C. McLennan and J. H. McLeod, Proc. Roy. Soc. **A115**, 515 (1927) (Direct observation).
[53] I. S. Bowen, Phys. Rev. **36**, 600 (1930); F. Paschen, Naturwiss. **18**, 752 (1930).
[54] Identified in Aurora by J. C. McLennan, J. H. McLeod and R. Ruedy, Phil. Mag. **6**, 558 (1928).
[55] Observed and identified by R. H. Stoy, Pub. A. S. P. **46**, 297 (1934).

stable states, ^2P, with relatively short lives and low level states ^2D with very long lives. As discussed for the last sequence, one would therefore expect large variations in the relative intensities of the groups of lines from these levels as the density of the source is changed.

Eight-electron systems. An energy diagram of Ne III which has a structure typical of these systems is shown in Fig. 3. All of the metastable states belong to the $2p^4$ configuration which gives rise to the same terms, ^3P, ^1D, ^1S, as the $2p^2$ configuration already discussed. The only difference between the two configurations is that in the present case ($2p^4$) the ^3P term is inverted, thus making the $^3P_2$ state the stable state of the atom. The predicted and observed wave-lengths are give in Table V. As in Table III, the $^3P_0-{}^1D_1$, $^3P_0-{}^1S$ and $^3P_2-{}^1S$ lines are omitted since their transition probabilities are such as to indicate that their intensities would be negligible in comparison with the other lines.

O I. Three of the forbidden lines of O I have been produced in the laboratory. The $^1D-{}^1S$ line was first observed by McLennan and Shrum* and later was obtained with an intensity sufficient for interferometer measurements of its wave-length.[52] Hopfield[51] has produced the $^3P-{}^1D$ lines. These directly observed wave-lengths are given in Table V in place of the less accurate calculated values. As in the six electron systems the low ^1D state has a very much longer lifetime (100 sec.) than the high ^1S state (0.5 sec.).

The $^1D-{}^1S$ line of O I at 5577.34A is the well-known green line that dominates the spectrum of the aurora and of the night sky. The $^3P-{}^1D$ is also present in the aurora but has a much lower intensity. All of these lines have also been observed in the nebulae but the relative intensities of the two groups are reversed, i.e., the $^3P-{}^1D$ pair is much stronger than the $^1D-{}^1S$ line. The explanation[53] of this great change in relative intensity is the same as that given for the behavior of the corresponding lines of O III and N II in the novae.

Indeed the metastable states of the p^2, p^3, and p^4 configurations, which include all of the metastable states of astrophysical interest in the first two rows of the periodic table, can be divided into two classes having very different characteristics. In the first class are the ^1D states of the p^2 and p^4 configurations and the ^2D states of the p^3 configuration. All of these terms have very long mean lives but have very low excitation potentials and high statistical weights. The lines corresponding to transitions from these levels are therefore the strongest lines of the ions involved under extreme low pressure conditions such as that found in the nebulae. In the second group are the ^1S states of the p^2 and p^4 configurations and the ^2P states of the p^3 configuration, all of which are characterized by high excitation potentials and low statistical weights but relatively short mean lives. Under conditions of moderately low pressure such as that found in the aurora or in the early stages of a nova the lines from this second group of levels are the strongest since their relatively high transition probability makes them less subject to effects of collisions or absorptions. These characteristic differences have led Boyce, Menzel and Payne[48] to suggest the name,

* J. C. McLennan and G. M. Shrum, Proc. Roy. Soc. **A108**, 501 (1925).

nebular lines, for the transitions from the first class. Transitions from the second class of levels were given the name auroral or trans-auroral depending on whether the transition was to the ^1D or ^2D states or to the ^3P or ^4S states.

F II. None of the lines of F II have been observed.

Ne III. The position of the $^1D-{}^1S$ line and the separation of the $^3P_1-{}^1D$ and $^3P_2-{}^1D$ lines can be predicted accurately from the analysis of the ultraviolet spectrum of Ne III. The wave-lengths of the latter pair can only be obtained approximately by an extrapolation from O I and F II. However the agreement between these predictions and the wave-lengths of the very strong pair of nebular lines at 3869 and 3968 as well as the behavior or these lines in the nebulae leaves little doubt as to the reality of the identification. The $^1D-{}^1S$ line falls so close to the position of a permitted O III line and a forbidden Cl III line that it cannot be resolved from them. In certain nebulae however Stoy[55] found a line at the proper wave-length, 3342A, when other oxygen lines were absent. The relatively weak intensity of this line may be due to the fact that the transition probability of $^3P_1-{}^1S$ is greater than that of $^1D-{}^1S$ in Ne III.

Na IV. Assuming the correctness of the above Ne III identifications, the Na IV $^3P-{}^1D$ lines, which are the only forbidden lines of this ion in the observable range, can be approximatedly located by extrapolation. The separation of these lines can be determined from direct observations in the extreme ultraviolet. The lines thus predicted are not found in the nebulae.

Mg V, Al VI, Si III. No forbidden lines of these elements occur in the observable range.

Nine-electron systems, F I, Ne II, Na III, etc. These atoms have no metastable states transitions from which can give rise to lines in the observable range.

Ten-electron systems, Ne I, Na II, Mg III, etc. While the $2p^53s^3P_0$ and $^3P_2$ states of these atoms are metastable, all forbidden transitions from them are in the extreme ultraviolet below 750A.

Eleven-electron systems, Na I, Mg II, Al III, etc. These atoms have no metastable states.

Twelve-electron systems, Mg I, Al II, Si III, etc. The $3s3p^3P_0$ and $^3P_2$ states of these atoms are metastable. Since the excitation potentials of the ^3P terms are all approximately the same, the only forbidden transitions from these metastable levels, $3s^2\,{}^1S-3s3p^3P_0$ and $3s^2\,{}^1S-3s3p^3P_2$, should always be accompanied by the permitted $3s^2\,{}^1S-3s3p^3P_1$ line which is situated between them. Since the $3s^2\,{}^1S-3s3p^3P_1$ line is an intercombination line its transition probability is also low and the $3s3p^3P_1$ state has therefore a fairly long-average life. However for these elements the departure from Russell-Saunders coupling is considerably greater than for the four-electron atoms with the result that the transition probability of this line is large enough to make its observation in the laboratory fairly easy. Its intensity would however be enhanced under extreme low pressure conditions.

Thirteen-electron systems, Al I, Si II, P III, S IV, etc. These atoms have no metastable state, transitions from which fall in the observable

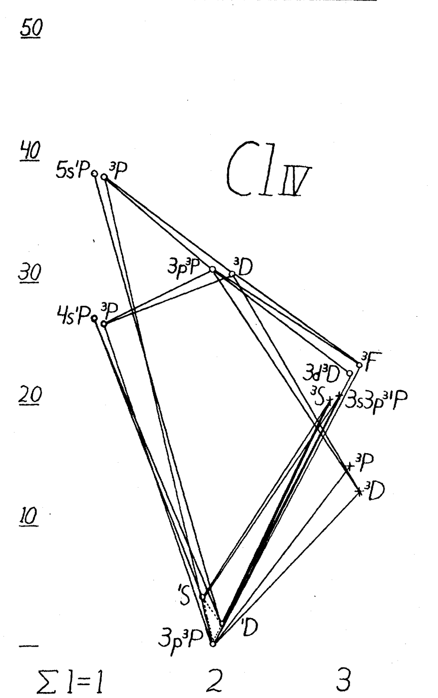


FIG. 4. Structure of a fourteen-electron system.

range. The $3s3p^2\,{}^4P$ state has a fairly long mean life and the intensity of the only transition from it, $3s^23p^2P-3s3p^2\,{}^4P$, should therefore be increased under nebular conditions. However this line is of no great astrophysical importance since, except for Al I, it is outside of the observable range and since its excitation potential is not appreciably lower than that of some of the permitted lines.

Fourteen-electron systems. The energy diagram of Cl IV in Fig. 4 shows the arrangement of the states in these atoms. The only metastable states of astrophysical interest are the ^1S, ^1D and ^3P terms of the $3s^23p^2$ configuration. All forbidden transitions from these terms that should have an appreciable intensity are listed in Table VI. The predicted wave-lengths are calculated directly from fairly complete analyses in the case of Si I, P II and Cl IV. The separations of the $^3P-{}^1D$ lines of the remaining ions are available from partial analyses of their spectra and the wave-lengths are determined by extrapolation or interpolation from adjacent elements.

Si I. Only one line of Si I falls in the observable range. Since this is a neutral atom one would not expect it to be abundant in the nebulae.

P II. The one line of P II that could appear in present lists of nebular lines is definitely missing.

S III. The $^1D-{}^1S$ line may correspond to the hitherto unidentified nebular line at 6313A. If

TABLE VI. *Fourteen-electron systems.*

		$^3P_1-{}^1D$	$^2P_2-{}^1D$	$^1D-{}^1S$	$^3P_1-{}^1S$	Excitation Potentials ^1D	S^1	Permitted
Si I	Calc.[56]				6526.88 ±0.1		1.9	5
P II	Calc.[57]			7869 ±3	4669.4 ±2		2.7	13
S III	Calc. Obs.	9070[58]	9533 ±8	6315 ±30[40] 6313?	3723 ±15[40]	1.4	3.3	21
Cl IV	Calc.[58] Obs.	7530.9	8046.1 ±8	5322.2 ±4	3118.3 ±2 3118?	1.7	4.0	31
A V	Calc.[40] Obs.[59]	6432 6435?	7003 ±50 7005?	4620 ±50		2.0	4.7	>42

[56] A. Fowler, Proc. Roy. Soc. **A123**, 422 (1929).
[57] H. R. Robinson, Phys. Rev. **49**, 297 (1936).
[58] I. S. Bowen, Phys. Rev. **46**, 377 (1934).
[59] Observed and identified by R. H. Stoy, Pub. A. S. P. **46**, 362 (1934).

TABLE VII. *Fifteen-electron systems.*

		$^4S-{}^2D_{1\frac{1}{2}}$	$^4S-{}^2D_{2\frac{1}{2}}$	$^4S-{}^2P_{\frac{1}{2}}$	$^4S-{}^2P_{1\frac{1}{2}}$	$^2D_{2\frac{1}{2}}-{}^2P_{\frac{1}{2}}$	$^2D_{2\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$	$^2D_{1\frac{1}{2}}-{}^2P_{\frac{1}{2}}$	$^2D_{1\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$	Excitation Potentials ^2D	^2P	Permitted
P I	Calc.[60]	8795.9	8783.9 ±8	5338.3	5331.1 ±3					1.4	2.3	8
S II	Calc.[61] Obs. A	6731.5 6730[62]	6717.3 ±4 6716[55]	4076.5 4076.22[62] 0.324	4068.5 ±2 4068.62 0.270					1.8	3.0	16
Cl III	Calc.[63] Obs.[59]	5537.7 5538	5517.2 ±4 5519	3353.4	3342.7 ±2 3342?[64, 55]	8550.5	8481.6	8501.8	8433.6 ±8	2.2	3.7	25
A IV	Calc.[65] Obs.[66]	4740.3 4740.2	4711.4 ±3 4711.4			7332.0	7236.0	7263.3	7169.1 ±5	2.6	4.3	35
K V	Calc.	4153[40]	4112 ±100			6446.5[67]	6316.6	6349.5	6223.4 ±5	3.0	4.9	47
Ca VI	Calc.	3703[40]	3646 ±200			5766.4[67]	5587.2	5631.0	5460.0 ±5	3.4	5.6	60

[60] C. C. Kiess, Bur. Standards J. Research **8**, 393 (1932).
[61] M. Gilles, Ann. de physique **15**, 267 (1931).
[62] I. S. Bowen, Nature **123**, 450 (1929).
[63] I. S. Bowen, Phys. Rev. **45**, 401 (1934).
[64] May also be Ne III or O III.
[65] J. C. Boyce, Phys. Rev. **48**, 396 (1935).
[66] P. Swings and B. Edlén, Comptes rendus **198**, 2071 (1934); J. C. Boyce, C. Payne-Gaposchkin and D. H. Manzel, Pub. A. S. P. **46**, 213 (1934).
[67] I. S. Bowen, Phys. Rev. **46**, 791 (1934).

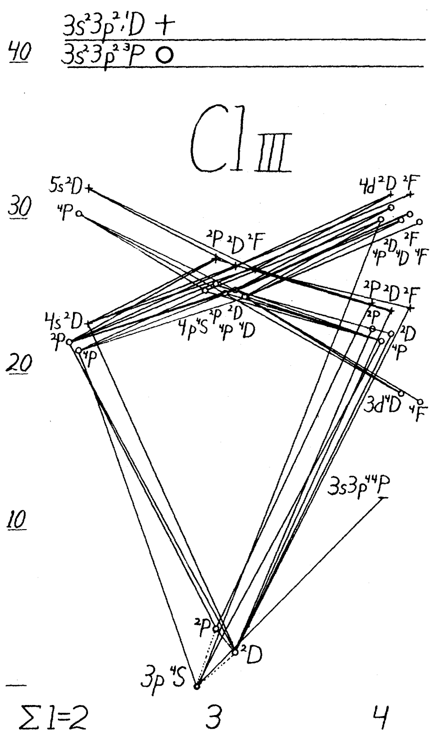


Fig. 5. Structure of a fifteen-electron system.

this identification is correct the ${}^3P_1-{}^1S$ line coincides with one of the high members of the Balmer series of H at 3722A.

Cl IV. The predicted position of the ${}^3P_1-{}^1S$ line agrees with the position of a faint nebular line at 3118. This line had been provisionally identified with a permitted line of O III.[36] However the agreement in wave-length with Cl IV is more satisfactory than with O III and the discovery of lines of other stages of ionization of Cl by Stoy[59] makes the attribution of this line to Cl IV seem more probable. The ${}^1D-{}^1S$ line predicted at 5322A is not observed. This may be due to the low sensitivity of plates in this region and to the fact that, for these heavier atoms, the ${}^3P_1-{}^1S$ transition becomes more probable than the ${}^1D-{}^1S$ transition.

A V. The ${}^3P-{}^1D$ pair may be represented by the nebular lines at 6435 and 7005A while the

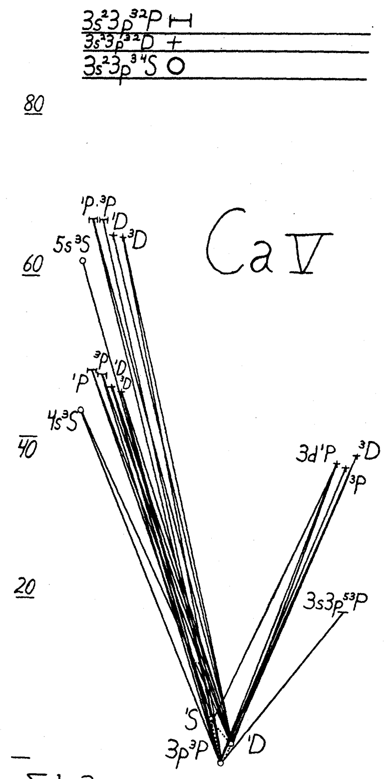


Fig. 6. Structure of a sixteen-electron system.

${}^1D-{}^1S$ line may be any one of a group of faint nebular lines near the predicted wave-length.

As may be seen in Fig. 4 certain terms of the $3d$ configuration are also metastable for all ions except Si I. All transitions from these levels are in the extreme ultraviolet however and are not therefore of astrophysical interest.

Fifteen-electron systems. Fig. 5 shows the energy diagram of Cl III which is a typical fifteen-electron system. Except for a few high level metastable states of the $3p^23d$ configuration, which are not of astrophysical interest, all metastable states are in the low $3p^3$ configuration. Of the terms of this configuration ${}^2P$ and ${}^2D$ are metastable while ${}^4S$ is the stable state. Possible transitions between these are listed in Table VII.

P I. As would be expected from the fact that this is a neutral atom and from the failure to find the P II lines in the nebulae, none of the forbidden lines of P I have been observed in nebulae or other objects.

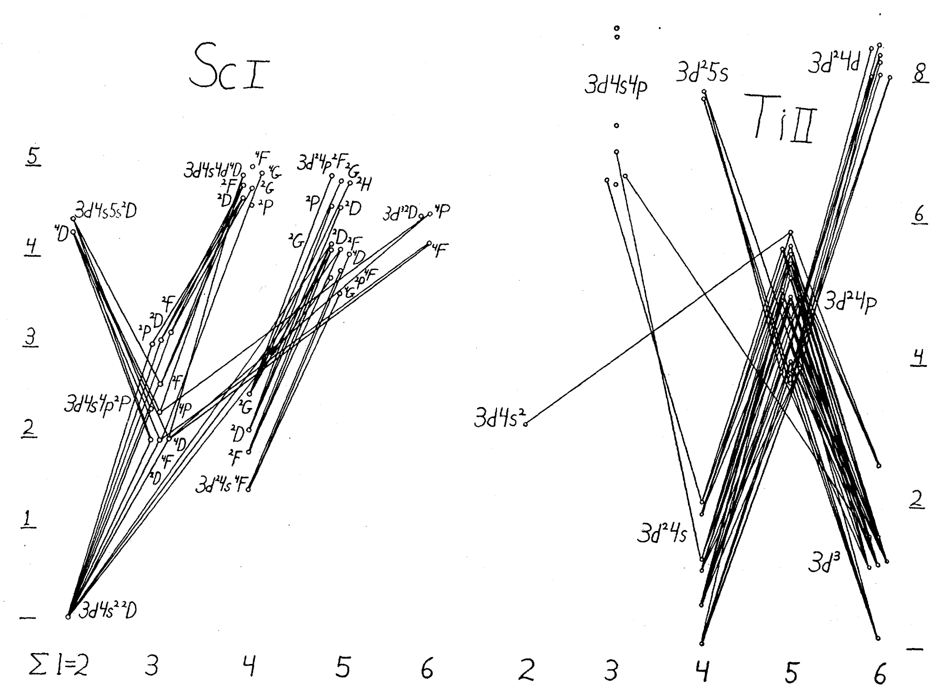
S II. All of the predicted lines of S II are definitely present in several nebulae.

Cl III. The $^4S-^2D$ lines are present, while the stronger of the $^4S-^2P$ lines is blended with a Ne III line as discussed under Ne III.

A IV. The one pair of lines in the range that has been observed is found in many nebulae.

K V and Ca VI. The lines from the high ^2P term are missing while the much stronger lines from the lower ^2D term are not accurately enough located to make possible a definite decision as to their presence. In any case lines of these high stages of ionization should be weak.

Sixteen-electron systems. Fig. 6 shows the arrangement of levels in Ca V which is a sixteen-electron system. The only metastable states of astrophysical interest are the ^1S, ^1D and ^3P terms of the $3p^4$ configuration. The forbidden transitions between these terms are listed in Table VIII. Unfortunately the analyses of these ions are far from complete. Thus the ^1S term has not been found in Cl II and K IV. In S I and A III its value is based on only one transition to the level, while in Ca V it is based on three. Since these values of the ^1S term in S I, A III and Ca V do not form a satisfactory progression, great doubt is thrown on part, at least, of these already very uncertain values. The wave-lengths of the $^3P_1-^1S$ and $^1D-^1S$ lines in Table VIII were obtained by neglecting the value of ^1S in A III and interpolating between the values in S I and Ca V. If this assumption is incorrect the tolerances indicated must be increased. On the other hand



A B

Fig. 7A, B.

the available analyses fix the positions of the $^3P-^1D$ lines quite unambiguously except in the case of Cl II for which the wave-lengths were obtained by interpolation. The exact separations of the $^3P-^1D$ lines are fixed by the analyses in all cases.

S I. The one line of S I that falls in the observable range, has not been observed.

Cl II. None of the lines of this ion are predicted with sufficient accuracy to make identification possible.

A III. The $^3P_2-^1D$ line, which should be the strongest forbidden line of this element, is probably represented by the nebular line in the extreme red at 7135.6A. The other component, $^3P_1-^1D$, falls beyond the range of wave-lengths that has been observed systematically in the nebulae, and furthermore has only about one-third of the intensity of the 7135.6A line. The other lines of A III cannot be predicted with sufficient accuracy to make an identification.

K IV. The strong $^3P_2-^1D$ transition may be represented by the faint nebular line at 6102A. As in A III the other component of this pair is fainter and is in a less completely observed region of the spectrum.

Ca V. Both components of the $^3P-^1D$ pair in Ca V correspond to observed lines in the nebulae and in Nova Pictoris. Contrary to predictions however the longer wave-length component, $^3P_1-^1D$, at 6087 is the stronger in both sources. In the late stages of Nova Pictoris this 6087 line is one of the two strongest lines in the spectrum. This makes this identification of the 6087 line, in particular, very doubtful.

Seventeen-electron systems, Cl I, A II, K III,

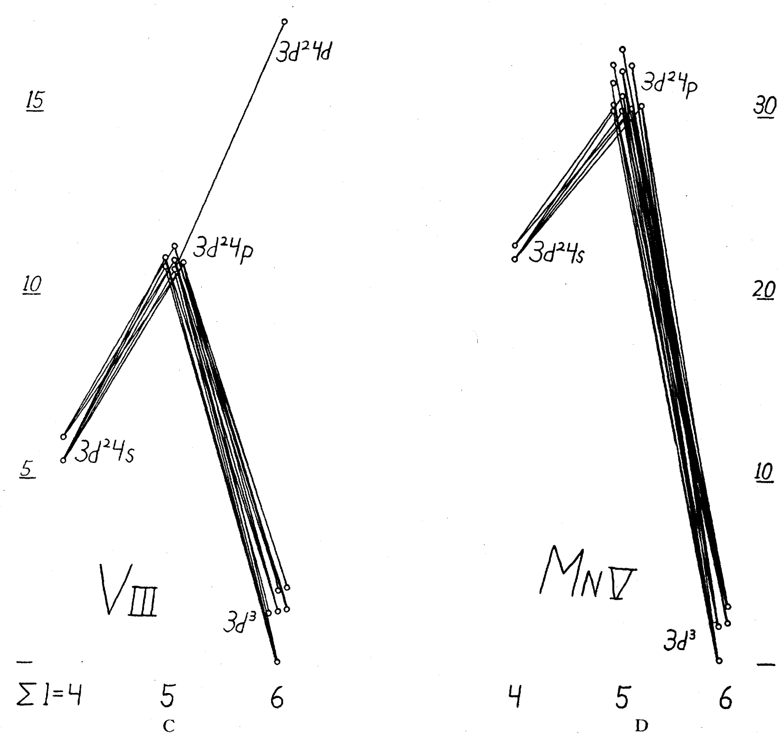


FIG. 7C, D. Structures of an isoelectronic sequence with three $3d$ and $4s$ electrons.

TABLE VIII. *Sixteen-electron systems.*

		$^3P_1-{}^1D$	$^3P_2-{}^1D$	$^1D-{}^1S$	$^3P_1-{}^1S$	Excitation Potentials ^1D	^1S	Permitted
S I	Calc.[68]			7724.4±3	4589.0±1		2.7	8
Cl II	Calc.[40]	9132	8589±200	6152±400	3676±200	1.4	3.4	16
A III	Calc.[69] Obs.	7751.0	7135.7±3 7135.6?	5187±500	3108±200	1.7	4.1	26
K IV	Calc. Obs.	6794.8[67]	6101.1±6 6102?[59]	4508±200[40]		2.0	4.8	>37
Ca V	Calc.[67] Obs.	6085.9 6085?[59]	5308.9±5 5313?	3996.3±5		2.3	5.4	>50

[68] J. E. Ruedy, Phys. Rev. **44**, 757 (1933). Ruedy's identification of $p^4\,{}^1S-p^3({}^2P)4s\,{}^1P$ has been changed to the line at 1782.25A to make the relationships of the terms of the p^4 configuration agree better with other atoms of similar structure.
[69] J. C. Boyce (Phys. Rev. **48**, 396 (1935); **49**, 351 (1936)) has made a tentative identification of a few singlet lines which give wave-lengths of 5597A and 3251A, for $^1D-{}^1S$ and $^3P_1-{}^1S$ respectively.

etc. and eighteen-electron systems, A I, K II, Ca III, etc. These systems have no metastable states, transitions from which can give rise to lines in the observable range.

As is at once evident from Tables III to VIII, all of the forbidden lines, in the observable range, of the elements in the first two rows of the periodic table have very low excitation potentials in comparison with the excitation potentials of the permitted lines of the same elements. Since these forbidden lines are therefore very much stronger than any of the permitted lines of the same elements, their presence or absence provides by far the most sensitive test for the presence of these elements in a nebula or other object with similar conditions of density.

Elements of the first long period K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni. In the group of elements from K to Zn the twelve $4s$ and $3d$ electrons are being filled in. Because of less complete screening by inner electrons a $4s$ electron is normally more stable, i.e., has a lower energy, in the neutral atoms of these elements. On the other hand as one progresses along an isoelectronic sequence to higher stages of ionization the energy of the lower-quantum-number, $3d$ electron decreases more rapidly with increasing atomic number than that of a $4s$ electron with the result that for high stages of ionization a $3d$ electron is more stable.

This is illustrated in Fig. 7 by the energy diagrams of the isoelectronic sequence of ions, Sc I, Ti II, V III, Mn V. In Sc I, the $3d4s^2$ configuration which has the maximum possible number of $4s$ electrons is the most stable configuration while the $3d^24s$ and $3d^3$ configurations have higher energies. in Ti II the $3d^24s$ configuration has become the most stable configuration with the $3d^3$ configuration only slightly above it. In the higher stages of ionization the $3d^3$ configuration sinks rapidly below all others and is by far the most stable configuration of the ions considered. Since the $4s^23d$, $4s3d^2$ and $3d^3$ configurations are all of even parity, i.e., the arithmetical sum of the l's is even, transitions between terms of these configurations are all forbidden. Consequently all terms of these configurations which lie below the lowest term of odd parity, i.e., the lowest term of either the $4s4p3d$ or $4p3d^2$ configurations are metastable.

Similarly for the general case of atoms with n electrons in these orbits, all terms of the even $4s^23d^{n-2}$, $4s3d^{n-1}$ and $3d^n$ configurations are metastable which lie below the lowest term of the odd $4s4p3d^{n-2}$ or $4p3d^{n-1}$ configurations. The forbidden lines of possible astrophysical interest correspond to the transitions between these low metastable terms of the $4s^23d^{n-2}$, $4s3d^{n-1}$ and $3d^n$ configurations. The permitted lines which have lowest excitation potentials and which are therefore the strongest lines in the laboratory spectrum of these ions correspond to transitions from the low odd $4s4p3d^{n-2}$ or $4p3d^{n-1}$ configurations. In Fig. 7 these permitted lines are represented by the solid lines. In going to the higher stages of ionization however these permitted lines progress into the ultraviolet outside of the astronomically observable range and this necessitates the use of lines of still higher excitation potential for direct identification of these ions in astronomical sources.

Because of complexity of the structure of these atoms many of them have a hundred or more possible forbidden transitions from metastable states in each stage of ionization. This makes it infeasible to list all of the possible forbidden lines in the observable range as was done for the first eighteen elements. Table IX however summarizes the present status of the analysis of these elements and indicates the spectral ranges where their forbidden lines are found. The elements are listed at the top of the table and the symbols indicating the stages of ionization in the first column at the left of the table.

TABLE IX. *Elements of the first long period.* B = 3000–5000A; Y = 5000–6667A; I = 6667–10,000A; C = Complete; NC = Nearly Complete; Inc = Incomplete; 0 = No Analysis.

	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I Neutral	– 2 C	– 2 C	YI 2 C	YI 2 C	YI 2 NC	BYI 3 Inc	Y 2 Inc	YI 2 NC	BYI 3 NC	BYI 3 C	I 4 C	— 4 C
II Singly Ionized		I 3 C	I 3 C	BYI 4 C	BYI 4 NC	BYI 6 Inc	I 5 Inc	BYI 5 NC[70]	YI 6 Inc	BYI 6 C	B 11 C	— 8 C
III Doubly Ionized			B 17 C	BI 19 C	BYI 20 NC	— 0	— 0	— 0	— 0	— 0	— 0	— 29 C
IV Trebly Ionized				— 29 C	YI 32 NC	— 0	— 0	— 0	— 0	— 0	— 0	— 0
V Quadruply Ionized					— 43 C	BYI 49 NC	BY 55 NC[71]	— 0	— 0	— 0	— 0	— 0
VI Quintuply Ionized						— 60 C	BYI 65 NC[72]	BY 70 NC[71]	— 0	— 0	— 0	— 0

[70] J. C. Dobbie, Proc. Roy. Soc. **A151**, 703 (1935).
[71] I. S. Bowen, Phys. Rev. **47**, 924 (1935).
[72] W. M. Cady, Phys. Rev. **43**, 322 (1933).

The highest symbol in the section for each stage of ionization gives the approximate location of the forbidden lines of the ion as they have been thus far determined. The symbol B indicates that forbidden lines are predicted in the region between 3000A and 5000A. This is the range in which photographic plates have their greatest sensitivity and hence astronomical observations of faint objects are most complete. Y indicates the presence of forbidden lines in the region from 5000A to 6667A. Panchromatic plates are sensitive in this region and an increasing amount of astronomical data is becoming available. I refers to the infrared region below 10,000A. Very few astronomical observations have been made in this region but the new infrared plates make these observations possible.

The second item in each section is the value of the lowest excitation potential, in electron volts, of any permitted line in the observable range. The strongest forbidden lines normally correspond to transitions to the lowest level of the atom or to levels only slightly above it. The excitation potentials of these forbidden lines are therefore proportional to the frequencies of the line and have values of 1.2 to 1.9, 1.9 to 2.5 or 2.5 to 4.2 electron volts for lines in the I, Y, or B regions of the spectrum, respectively. From the table it is evident that the excitation potential of the permitted lines is only slightly above that of the forbidden lines in the cases of the neutral atoms. In the singly-ionized atoms the difference between the excitation potentials of the permitted and forbidden lines has increased although the excitation potentials are still of the same order of magnitude. Therefore, even under nebular conditions, one would not expect the forbidden lines of these stages of ionization to become appreciably stronger than the permitted lines as was the case for the elements of the first two rows of the periodic table. If the permitted lines of one of these neutral or singly ionized atoms are missing from the spectrum of a given object, the forbidden lines of that ion will not appear with a high intensity.

In the higher stages of ionization, however, the excitation potentials of the forbidden transitions between the terms of the very low $3d^n$ configuration are very much lower than that of any permitted line. These higher stages of ionization behave therefore like the elements of the first two rows of the periodic table in that their forbidden lines may be very strong in comparison with the permitted lines.

The third and lowest item in the last section of the table indicates the completeness of the analysis of the low metastable states that are necessary for the prediction of the position of the forbidden lines of these elements. C signifies that the analysis is essentially complete and lacks at most a term or two of low multiplicity such as a singlet. The designation NC is given when the analysis is nearly complete and has fixed all of the important terms, combinations between which are likely to give rise to strong forbidden lines. In this case several metastable terms usually of low multiplicity may be missing. Inc **indicates** that enough metastable terms have been found to locate the position of one or more important groups of forbidden lines but that the analysis is still quite incomplete in important details. An O means that not enough of the metastable states have been located to determine the position of any forbidden transition in the observable range. In all cases where a reference is not indicated the analysis is given by Bacher and Goudsmit.[73]

From this table it is evident that the analyses are fairly complete in the cases of the relatively simple spectra obtained when there are not more than three electrons in these orbits. Likewise a satisfactory analysis of the spectra of all neutral and singly-ionized atoms has been made possible by the availability of interferometer or other very accurate measurements and of Zeeman patterns of the lines of these atoms. On the other hand all of the higher stages of ionization having four or more electrons in these orbits are practically unanalyzed. Unfortunately, as pointed out above, it is just these higher stages of ionization that are of especial importance since the forbidden lines of these ions may be very strong without the appearance of any of the permitted lines to indicate the presence of the ion concerned.

These highly ionized atoms of Cr, Mn, Fe, Co, Ni, Cu and Zn are practically the only ions of great astronomical abundance whose forbidden lines cannot be predicted at least approximately from analyses now available. It is therefore to be expected that, when the analyses of these highly ionized atoms are made, it will be possible to classify many of the outstanding unidentified

TABLE X. *The forbidden lines of Fe II in η Carinae.*

		$a^6D_{4\frac{1}{2}}$	$a^6D_{3\frac{1}{2}}$	$a^6D_{2\frac{1}{2}}$	$a^6D_{1\frac{1}{2}}$	$a^6D_{\frac{1}{2}}$
$b^4P_{2\frac{1}{2}}$	Int. Obs.		[3]			
	Calc.	4799.31	4889.63	4958.22	5006.64	5035.48
	Obs.		4889.50			
$b^4P_{1\frac{1}{2}}$	Int. Obs.			[5]		
	Calc.		4665.66	4728.07	4772.07	4798.27
	Obs.			4728.05		
$b^4P_{\frac{1}{2}}$	Int. Obs.				[2]	
	Calc.			4598.07	4639.68	4664.45
	Obs.				4639.64	
$b^4F_{4\frac{1}{2}}$	Int. Obs.	[9]	[3B]			
	Calc.	4416.28	4492.64	4550.48		
	Obs.	4416.38	4491.71			
$b^4F_{3\frac{1}{2}}$	Int. Obs.	[0]	[5]	[5B]		
	Calc.	4382.76	4457.95	4514.90	4555.01	
	Obs.	4382.34	4457.90	4515.19		
$b^4F_{2\frac{1}{2}}$	Int. Obs.			[3B]		
	Calc.	4358.11	4432.45	4488.75	4528.39	4551.98
	Obs.			4488.93		
$b^4F_{1\frac{1}{2}}$	Calc.		4414.46	4470.29	4509.61	4533.00
$a^6S_{2\frac{1}{2}}$	Int. Calc.	100.0	80.0	60.0	40.0	20.0
	Int. Obs.	10.0	B	5.4	3.5	1.6
	Calc.	4287.41	4359.34	4413.78	4452.11	4474.91
	Obs.	4287.31	4359.11	4413.80	4452.02	4474.73

		$a^4F_{4\frac{1}{2}}$	$a^4F_{3\frac{1}{2}}$	$a^4F_{2\frac{1}{2}}$	$a^4F_{1\frac{1}{2}}$
$b^4P_{2\frac{1}{2}}$	Int. Calc.	100.0	32.0	7.2	0.8
	Int. Obs.	(5)			
	Calc.	5273.38	5433.15	5556.31	5643.99
	Obs.	5274.9			
$b^4P_{1\frac{1}{2}}$	Int. Calc.		48.0	34.1	11.2
	Int. Obs.		(5B)		
	Calc.		5158.02	5268.89	5347.67
	Obs.		5159.5		
$b^4P_{\frac{1}{2}}$	Int. Calc.			18.7	28.0
	Calc.			5107.96	5181.97
$a^4H_{6\frac{1}{2}}$	Int. Calc.	100.0			
	Int. Obs.	(5B)			
	Calc.	5158.81			
	Obs.	5159.5			

		$a^4F_{4\frac{1}{2}}$	$a^4F_{3\frac{1}{2}}$	$a^4F_{2\frac{1}{2}}$	$a^4F_{1\frac{1}{2}}$
$a^4H_{5\frac{1}{2}}$	Int. Calc.	11.4	74.3		
	Int. Obs.		(2)		
	Calc.	5111.64	5261.62		
	Obs.		5263.5		
$a^4H_{4\frac{1}{2}}$	Int. Calc.	0.79	14.5	56.1	
	Int. Obs.			(2)	
	Calc.	5072.42	5220.07	5333.66	
	Obs.			5337.6	
$a^4H_{3\frac{1}{2}}$	Int. Calc.	0.02	1.00	11.2	44.9
	Int. Obs.				(0)
	Calc.	5039.11	5184.81	5296.85	5376.48
	Obs.				5374.3
$b^4F_{4\frac{1}{2}}$	Int. Calc.	100.0	28.6	2.3	
	Int. Obs.	[5]	(0)		
	Calc.	4814.56	4947.39	5049.30	
	Obs.	4814.50	4948.7		
$b^4F_{3\frac{1}{2}}$	Int. Calc.	28.6	41.6	31.6	3.0
	Int. Obs.	[0]	[0]		
	Calc.	4774.75	4905.36	5005.52	5076.58
	Obs.	4774.62	4905.44		
$b^4F_{2\frac{1}{2}}$	Int. Calc.	2.3	31.6	20.4	24.2
	Int. Obs.		[0]		
	Calc.	4745.50	4874.50	4973.40	5043.53
	Obs.		4874.83		
$b^4F_{1\frac{1}{2}}$	Int. Calc.		3.0	24.2	25.1
	Calc.		4852.74	4950.75	5020.25
$a^4G_{5\frac{1}{2}}$	Int. Calc.	100.0	15.4		
	Int. Obs.	8.0	1.0		
	Calc.	4243.98	4346.86		
	Obs.	4243.93	4346.68		
$a^4G_{4\frac{1}{2}}$	Int. Calc.	21.6	55.6	18.9	
	Int. Obs.	0.6	3.4	(B)	
	Calc.	4177.21	4276.84	4352.79	
	Obs.	4177.39	4276.80	4352.10	
$a^4G_{3\frac{1}{2}}$	Int. Calc.	1.94	25.4	35.4	14.1
	Int. Obs.		0.9	1.7	0.8
	Calc.	4146.67	4244.82	4319.63	4372.44
	Obs.		4245.35	4319.62	4372.49
$a^4G_{2\frac{1}{2}}$	Int. Calc.	0.05	2.45	19.9	35.3
	Int. Obs.			0.8	(B)
	Calc.	4134.02	4231.57	4305.90	4358.38
	Obs.			4305.76	4359.11

[73] R. F. Bacher and S. Goudsmit, *Atomic Energy States*, (McGraw-Hill Book Co.).

lines in the novae and possibly in the corona. Thus the fact[74] that the chief coronal lines appeared in R S Ophiuchi at approximately the same time as the forbidden lines of O and Ne, points to the classification of the coronal lines as forbidden lines. Since the only permitted transitions to the metastable states of these highly ionized atoms fall in the extreme ultraviolet, the atoms would not be rapidly removed from these states by absorption of solar radiation. Consequently the forbidden lines of these high stages of ionization may appear with great intensity near the surface of the sun even though, as discussed in Section V, the forbidden lines of the lower stages of ionization of the same element cannot.

The forbidden lines of these elements that have thus far been observed in astronomical sources are those of Fe II and possibly of Fe VI. The lines of Fe II were first identified by Merrill[75] in the spectrum of η Carinae. These lines have also appeared in the spectra of several novae. The observed multiplets of Fe II are listed in Table X. The calculated intensity gives the intensity of each line relative to that of the strongest line of the multiplet as given by the formulae developed by Rubinowicz.[14] The observed intensities in square brackets are estimates by Moore and Sanford[75] and in parentheses by Jones.[76] The values without parentheses represent quantitative measures by Merrill and Burwell of the Moore and Sanford plates. In Fe VI, the ${}^4F_{3\frac{1}{2}}-{}^2G_{4\frac{1}{2}}$, ${}^4F_{3\frac{1}{2}}-{}^2G_{3\frac{1}{2}}$, and ${}^4F_{4\frac{1}{2}}-{}^2G_{4\frac{1}{2}}$ lines are predicted at wave-lengths of 4968.8, 5146.8 and 5177.0A, respectively. Fairly strong lines have appeared in the spectrum of Nova Pictoris[77] at 4968.1, 5148.5 and 5176.3A.

The analysis of the elements beyond Zn are on the whole even more incomplete than those of the first long period. However none of the heavier elements have an astronomical abundance comparable with most of the elements lighter than Zn. It is therefore very unlikely that the lines of these rare elements would appear in any strength in the faint objects where the forbidden lines are normally observed.

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